Gas venting and hydrate deposits in the Okhotsk Sea

R. E. CRANSTON, G. D. GINSBURG, V. A. SOLOVIEV & T. D. LORENSON

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Active gas vents and methane hydrate deposits were found in two areas of the Okhotsk Sea in October, 1991 onboard the *R. V. Antropov*, a Russian research vessel operated by Dalmorgeologia from the Far-East Region of Russia. Gas vents were identified in water depths of 700 to 800 m using a 20 khz fish finding echo sounder. Sediment and hydrate samples were recovered using a 3 m long gravity corer. Some cores contained 30 to 40% by volume methane hydrate in lenses, layers and veins.

A small fraction of the venting gas is captured in a methane hydrate phase, while a majority of the vented gas is released and dispersed in the overlying seawater. Small gas bubbles were observed at the sea surface, indicating that some of the venting gas reaches the atmosphere directly.

Preliminary hydrocarbon gas and methane isotopic composition suggest that the venting gas is biogenic in origin. Based on the flux of organic carbon reaching the seafloor and pore water ammonia results, recent biogenic processes are not sufficient to support the production of the venting methane. It is concluded that biogenic methane from subsurface sediment layers is migrating upwards along preferential pathways associated with faulting.

R. E. Cranston, Geological Survey of Canada, Box 1006, Dartmouth, N.S., B2Y 4A2, Canada. G. D. Ginsburg, & V. A. Soloviev, Research Institute for Geology and Mineral Resources of the Ocean, Maklina pr.1, 190121, St. Petersburg, Russia. T. D. Lorenson, U.S. Geological Survey, 345 Middlefield Road, MS-999, Menlo Park, CA 94025 U.S.A. September 17th, 1992.

Introduction

Methane vents and gas hydrate deposits are important as sources and sinks when considering the global marine methane budget. Methane is released to the ocean from biogenic, thermogenic and primordial sources originating from the sea floor (Cranston, 1993). Gas hydrates are specialized mixtures of free gas and water that occur in a frozen state, under pressure and temperature conditions often found along coastal margins (e.g. >400 m water depths, water temperature <5°C) (Sloan, 1989). Methane hydrates contain up to 180 L of methane (STP) in one litre of hydrate. In addition to being the largest reservoir in the global methane budget (Kvenvolden 1988), hydrate deposits can become unstable when temperatures rise and/or overburden pressure decreases. During past ice ages, it is speculated that gas hydrates melted when sea level dropped, and/or as ice sheets lifted off shelf sediments, thus lowering the total pressure exerted on the deposits (Paull and Ussler, 1991; Solheim and Elverhøi, 1993). Because methane is an effective greenhouse gas, and the concentration is known to have risen significantly toward or at the end of ice ages (Stauffer et al., 1988; Raynaud et al., 1988), it has been proposed that hydrate melting had a role in warming the atmosphere which

stopped glaciation and/or enhanced the rate that glaciers retreated (Paull and Ussler, 1991; Nisbet, 1989). Understanding the distribution and stability of gas vents and hydrate deposits, and their role in global carbon processes in the past and present is essential to reduce uncertainty in global change research.

Zonenshayn et al. (1987) described the discovery of methane vents and gas hydrate deposits in the eastern Okhotsk Sea. Based on this and additional information about methane in bottom water near Sakhalin Island in the Okhotsk Sea (Obzhirov, 1992), a expedition to study gas venting and hydrate deposits was carried out in the Okhotsk Sea in October, 1991 using the *R. V. Geolog Pyotr Antropov*.

Sampling and analytical methods

Navigation fixes were obtained using a GPS Navstar positioning system, with precision and accuracy estimated to be ± 15 m. A 20 khz echo sounder, normally used as a fish finding tool, was used to locate gas venting sites. Sediment cores were extracted from the sea floor with a 10 cm diameter, 3 m long gravity corer fitted with a polyethylene liner. Some gas hydrate samples were
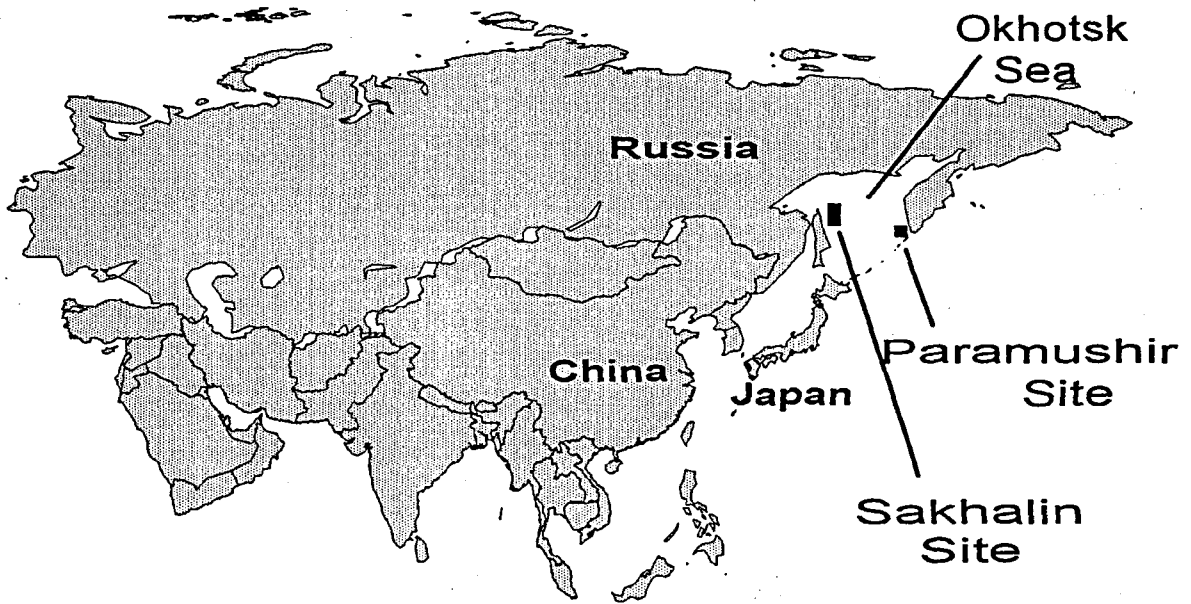
Fig. 1. Map of study area.

allowed to melt in containers filled with salt water. Gas bubbles from the hydrate were collected by displacing salt-saturated water in glass bottles and by vacutainers. Some hydrated samples were analyzed onboard for C_1-C_4 hydrocarbon gases while others were returned to land-based laboratories for C_1-C_5 hydrocarbon and methane isotopic analyses. Wet sediment subsamples were collected for dissolved and solid phase geochemical analy-

ses. Pore water samples were recovered by squeezing wet sediment in stainless steel compression chambers.

Pore water samples were analyzed onboard immediately to minimize sample storage problems. Combination electrodes were used to measure pH and eH, while chlorinity was determined using a silver nitrate titration. Dissolved sulfate was analyzed in pore waters using a barium sulfate precipitation/turbidimetric method. Ammonia and
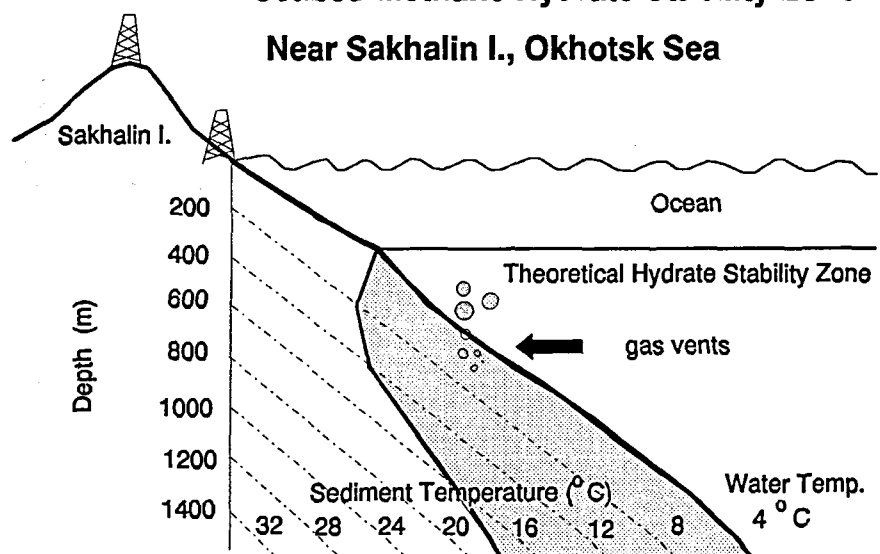

Fig. 2. Hydrate stability zone for offshore region near Sakhalin Island.

Table 1. Geochemical Results for Hydrated and Non-hydrated Sediment Samples

no. obs.	Non-hydrated Samples 11 (mean ± std. dev.)	Hydrated Samples 3 (mean ± std. dev.)	2-tailed t-test (% Probability means are different)
Sediment			
subsample			
depth (cm)	70±73	95±25	–
Si (%)	31.7±2.8	32.1±0.8	–
Al (%)	4.8±0.6	5.2±0.2	–
Ca (%)	1.7±2.7	0.7±0.1	–
Fe (%)	2.06±0.10	2.09±0.04	–
Mg (%)	0.30±0.09	0.27±0.02	–
K (%)	1.37±0.20	1.47±0.71	–
Mn (ppm)	43±41	41±35	–
Zn (ppm)	101±16	82±5	>99
Li (ppm)	23±4	18±3	–
Cu (ppm)	31±12	33±4	–
Cr (ppm)	30±4	26±4	–
Ni (ppm)	12±4	10±6	–
or. carb. (%)	1.45±0.22	1.27±0.08	>95
sand (%)	4±1	3±2	–
silt (%)	52±2	53±2	–
clay (%)	44±1	44±3	–
water (%)	61±3	65±1	>99
Pore Water			
pH	8.0±0.3	8.1±0.1	–
eH (mv)	−90±220	−320±60	>99
Si (mM)	0.8±0.2	0.7±0.3	–
Sulfate (mM)	10±3	0±0	>95
Ammonia (mM)	1.0±1.1	0.8±0.8	–
Chlorinity (g/L)	18.4±0.4	11.7±3.7	>95

silica were determined using routine nutrient colorimetric methods.

On land, sediments were freeze-dried and analyzed for organic carbon using a Leco WR-112 carbon analyzer and for total metals by decomposing the samples with hydrofluoric acid and aqua regia, followed by atomic absorption measurements. Sand-sized particles were recovered with a 63 μm sieve, while silt and clay fractions were measured with a Coulter Counter particle counter.
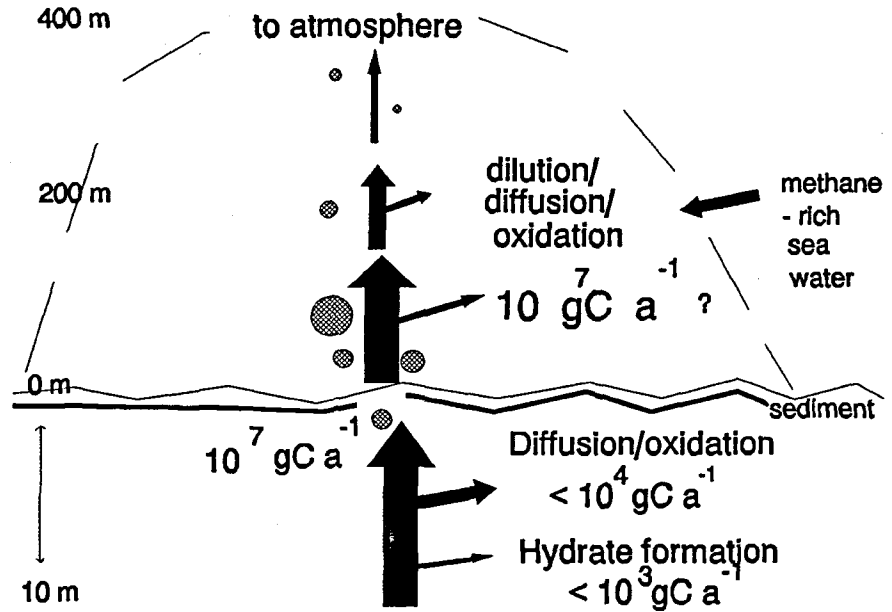
Results

Analytical results for shipboard and land laboratory studies are available in Cranston (1991) and Cranston and Standing (1992). A detailed description of gas vents and hydrate characteristics is available in Ginsburg et al. (1993).

A total of 10 new active gas vents were identified in the western Okhotsk Sea off the northeast coast of Sakhalin Island, along with one vent that was reported by Zonenshayn et al. (1987) near Paramushir Island on the east coast of the Okhotsk Sea (fig. 1). The sea floor footprint of the gas vents appear to be 100 to 300 m in diameter. Gas plumes that rose hundreds of metres above the sea floor could be observed on the 20 Khz fish finding sonar. Small gas bubbles (estimated to be 1 mm in radius) were observed at the sea surface 700 m above one vent when the sea was extremely calm. It is not known whether methane bubbles routinely reach the sea surface as the small bubbles may not be visible under normal sea conditions.

Gas hydrate samples, found in both study areas (fig.1), were collected in 7 cores and were inferred from pore water analyses in 4 additional cores. Figure 2 is a schematic of the Sakhalin Island region, showing that the recovered hydrates were found well within the hydrate stability zone. Stability zone data are calculated for pure methane in pure water, using software available in Sloan (1989). Subsurface sediment temperatures are based on the geothermal gradient (1 to 4°C per 100 m) measured during the expedition (Cranston, 1991). The hydrate occurred in layers (millimetres to centimetres thick) in the upper 2 metres of the sediment column. If minor amounts of hydrates are not visible, they can be identified by a temperature drop in the core as the hydrate melts (latent heat of fusion for hydrates is similar to normal ice), by visual gas disturbance of the sediment layers, and by measuring the salinity of the pore water, since water from hydrate contains very little salt, and as the hydrate melts, the surrounding pore water is diluted. Hydrated cores had

Fig. 3. Methane budget at a single bubble gas vent.

400 m

to atmosphere

dilution/ diffusion/ oxidation

10^7 gC a^{-1} ?

methane - rich sea water

200 m

0 m

sediment

10^7 gC a^{-1}

Diffusion/oxidation

$< 10^4$ gC a^{-1}

Hydrate formation

$< 10^3$ gC a^{-1}

10 m

to be processed immediately, as the hydrated melted within 45 minutes of removing the corer from the sea floor. Gas captured from the hydrate contained 97% methane, 2% carbon dioxide, 30 ppmv ethane, 15 ppmv propane, 5 ppmv n-butane, and 2 ppmv i-butane. Isotopic composition was: $\delta^{13}C_{CH_4}$ = −60 to −67‰; $\delta^{13}C_{CO_2}$ = −24.9‰; δD_{CH_4} = −207‰. Based on the hydrocarbon gases and isotope results, it is concluded that the hydrate methane is biogenic in origin.

Hydrates were found in 3 of 15 subsamples collected with a 250 m radius at one vent site off Sakhalin Island (fig. 1). Mean geochemical concentrations for the hydrated and unhydrated samples are compared in Table 1. These comparisons were done to determine whether geochemical characteristics vary between hydrated and non-hydrated samples. A statistical t-test was applied to determine whether the means are significantly different. Of the 24 variables compared in Table 1, only 6 pairs of means are significantly different at >95% probability. Hydrated samples tend to have higher water content and lower chlorinities due to melting of hydrates during sample handling and dilution of the surrounding pore water. Dissolved sulfate and redox potential are lower in hydrated samples than in non-hydrated samples. Venting methane plays a role in consuming oxidants, including sulfate, thus making the immediate environment more reducing. It is interesting that many of the geochemical measurements appear to be similar for the two types of samples, including major and trace elements and particle size. It is not clear why organic carbon and zinc appear to be depleted in the hydrated samples. Detailed chemical speciation work is required to understand these differences.

Discussion

Methane Budget at Vent Site

Based on submersible observations at the Paramushir site, individual vent holes released on the order of 1 bubble per second, with a bubble radius of 1 cm, and the bubble vents 2 m apart (Zonenshayn et al., 1987). For a water depth of 700 m and bottom temperatures of 4°C, it can therefore be calculated that a single bubble vent releases on the order of 10^7 gC a^{-1} as methane. Figure 3 depicts the important sinks for the methane as it bubbles through the sediment and water columns before it reaches the atmosphere. Within the sediment column, a portion of the venting methane is oxidized, some diffuses horizontally into surrounding sediments, and some is captured as methane hydrate. In the water column, gas bubbles rise upward, with some portion dissolving, diffusing and oxidizing.

Quantitative order of magnitude estimates of some of these sinks can be made. Since the single-bubble vents are estimated to be about 2 m apart (see above), it is assumed that there is a vertical 'chimney' of sediment, with a 1 m radius, around each vent. Oxidation of methane has been estimated to be on the order of 1 mmole methane m^{-2} d^{-1} (Alperin & Reeburgh, 1985; Devol, 1983; Iversen and Jørgensen, 1985). Thus, within a 1 m radius sediment column, this process could oxidize on the order of 10^1 gC a^{-1}.

Diffusion away from the vent tube into the 1 m radius sediment chimney would also capture some of the venting gas. Assuming a concentration change of 100 mM (order of magnitude for solubility of methane at a pres-

sure of 70 atm and temperature of 4°C) over a horizontal distance of 1 m, and a methane diffusion coefficient of 10^{-5} cm^2 s^{-1} (Devol, 1983), the horizontal diffusive flux away from the vent tube is 40 g C m^{-2} a^{-1}. If the height of the cylinder is between 1 to 100 m high, the surface area of the cylinder is 3 to 300 m^2. Thus, the horizontal, diffusive transport of methane away from the vent tube is between 10^2 to 10^4 gC m^{-2} a^{-1}.

The sink due to hydrate formation is unknown, but because the hydrated zones do not form mounds above the normal surrounding sediments, it can be assumed that the vertical growth rate of the hydrate is less than the sedimentation rate, which was estimated to be on the order of 10 cm ka^{-1} (Zonenshayn et al., 1987). If the 1 m radius chimney around a single vent accumulates 10 cm of hydrated sediments in 1000 years, with an average hydrate content of 50% on a volume basis, this would allow on the order of one litre of methane hydrate to collect in each sediment chimney, or this would capture $<10^2$ gC a^{-1} methane at each vent site.

In summary, oxidation could capture 10^1 gC a^{-1} around a vent tube, horizontal diffusion could transport 10^2 to 10^4 gC m^{-2} a^{-1}, and hydrate formation could capture $<10^2$ gC a^{-1} at each vent site. All three sinks in the sediment are minor relative to the single-vent release estimated to be 10^7 gC a^{-1}.

As the venting gas escapes from the sediment, oxidation and horizontal transport (via diffusion and advection) in the water column consumes some of the methane. Diffusive and advective fluxes could transport all of the released methane many kilometres away from the vent each year. Oxidation of methane in the water column will also consume a portion of the venting gas. Any estimate of methane sinks in the water column can vary by many orders of magnitude, however it is sufficient to conclude that horizontal transport away from the vent plume could consume all of the venting gas, thus eliminating the release of methane to the atmosphere. As was mentioned above, bubbles (1 mm radius) were observed during extremely calm sea conditions at the Sakhalin site. It appeared that some portion of the gas was reaching the atmosphere.

Carbon Budget Considerations

Based on gas analyses and estimates of vent release rates made earlier, it is concluded that biogenic methane is escaping at a rate of about 10^7 gC a^{-1} at each single vent hole. Assuming that each bubble path is surrounded by a 1 m radius 'chimney' of sediment, the flux of methane from the sea floor, for each vent site, is on the order of 10^6 gC m^{-2} a^{-1}. How does this compare to the amount of organic carbon that is being deposited at the site? Using order of magnitude results, it is known that the organic carbon content for these sediments is 1% in the vent region (Cranston and Standing, 1992; table 1) and the sedimentation rate is 10 cm ka^{-1} (Zonenshayn, 1987). The water content of wet sediment for these sediments is

50–65% (Cranston, 1991; table 1). By multiplying the organic carbon content and the sedimentation rate, and adjusting for water content, the carbon burial flux at the vent site is calculated to be on the order of 1 gC m^{-2} a^{-1}. Present day remineralization of organic carbon can be estimated by considering the ammonia gradient, since for every 7 moles of organic carbon that is oxidized in the sediment, 1 mole of ammonia is released (Christensen et al., 1987). The average ammonia gradient was found to be 1 mM m^{-1} (Cranston, 1991). Multiplying the apparent diffusion coefficient for ammonia of 10^{-6} cm^2 s^{-1} (Christensen et al., 1987) by the ammonia gradient, and correcting for a carbon/nitrogen ratio of 7, it is found that the approximate amount of organic carbon remineralization in the shallow sediment column is on the order of 10^{-1} gC m^{-2} a^{-1}.

Based on the calculations and estimates shown above, it is concluded that the amount of organic carbon being released from the sediment column (10^6 gC m^{-2} a^{-1}), in the form of biogenic methane, is many orders of magnitude larger than the amount of organic carbon that is being buried at the vent site (1 gC m^{-2} a^{-1}) and the amount of organic carbon that is being remineralized in the upper 1 m of the sediment column (10^{-1} gC m^{-2} a^{-1}). In order for this imbalance to persist, the biogenic methane must come from deeper in the sediment column. It is migrating from deposits where buried organic matter has been converted into methane and the methane is migrating horizontally through permeable layers, until preferential vertical pathways in the sediment structure are found. The collected gas migrates upward along fault pathways and is expelled from the sea floor.

Conclusions

We have made rough estimates of the methane flux from an active gas vent, however further research is required to balance the methane budget. Sea floor flux measurements and observations are required to quantify the release rate per vent hole and per unit area. Methane consumption processes such as diffusion, oxidation and hydrate formation need to be directly measured. Since the Okhotsk Sea is ice-covered for a portion of the year, water sampling under the ice needs to be done to determine how much methane is able to pass through the water column reach the atmosphere. Air sampling in this region during ice breakup in the spring may provide valuable data to understand the atmospheric methane budget.

Dansk sammendrag

Aktive gasudslip og forekomsten af gashydrater blev fundet i to områder i det Othotske Hav i oktober 1991. Gasudslippene blev observeret i de overfladenære sedi-

menter på vanddybder mellem 700 til 800 meter ved hjælp af et 20khz ekkolod. Sedimentprøver indeholdende gashydrater blev indsamlet med en 3 m lang kernetager af stødlodtypen. Enkelte kerner indeholdt op til 40 vol% gashydrat i form af mindre lag, linser og årer.

Gassen består hovedsagelig af methan (97%), kuldioxid (2%) og mindre mængder af tungere kulbrinter. Analyser af kulstof-isotopsammensætningen af den indsamlede methan og kuldioxid tyder på, at gassen har en biogen oprindelse. Imidlertid er mængden af organisk kulstof i de recente overfladenære sedimenter ikke tilstrækkelige til at forklare størrelsesordenen af gasproduktion fra de to gasudslip. Det må derfor formodes, at gassen stammer fra dybereliggende aflejringer med relativt stort organisk indhold, og at den strømmer op til overfladen i forbindelse med lokale forkastningssystemer.

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